Piano-Stool N-Heterocyclic Carbene Iron Complexes: Synthesis, Reactivity and Catalytic Applications

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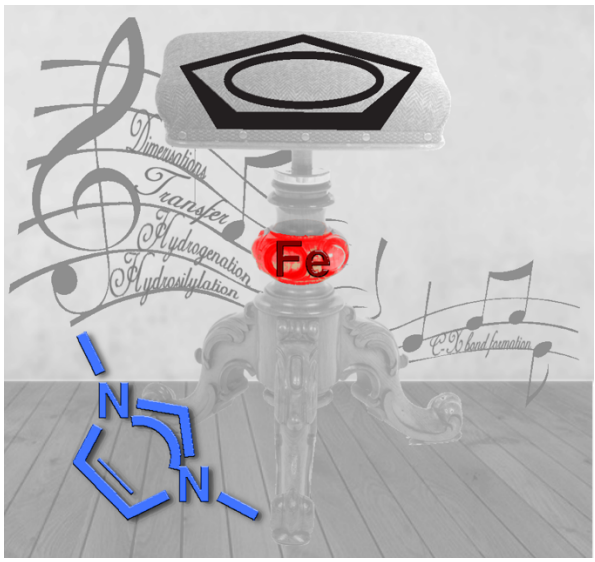
Abstract. This review summarises the advances of N-heterocyclic carbenes (NHCs) as ligands to iron half-sandwich complexes, often referred to as piano-stool complexes because of their structural motif. The review introduces various synthetic routes towards this sub-class of NHC iron-complexes including in particular direct and transmetallation strategies as well as the synthesis of the carbene directly within the iron coordination sphere. Many of these complexes have demonstrated promising reactivity that is relevant to the arenas of catalysis and materials chemistry. In particular, bond activation (*e.g.* C–H, Si–H, H–H) processes provide exciting new opportunities to exploit these systems for stoichiometric and catalytic transformations. Substantial advances have been achieved specifically in the catalytic reduction of unsaturated substrates, and this topic is emphasised in particular.



Content

1. Introduction

In recent years, developing catalysts based on cheap, Earth-abundant and environmentally benign transition metals has become an area of intense research.[1-11] While historically disregarded in favour of rare and precious metals, iron fulfils all these requirements and furthermore supports a plethora of catalytic transformations including substitution and addition reactions, isomerisations and rearrangements, and oxidation and reduction reactions.[10,12] This broad scope is in part attributed to the extensive range of oxidation states available to iron, from −2 to +6. Furthermore, iron can emulate the standard two-electron processes typical for the noble metals, but can also partake in single-electron transfer (SET) reactions which opens up the potential for an array of radical transformations. The ever increasing popularity of redox non-innocent[7] and cooperative ligands[11] is expected to create new and exciting opportunities within the arena of iron catalysis.

Since they were first isolated in 1991 by Arduengo and co-workers,[13] N-heterocyclic carbenes have emerged as powerful ligands in organometallic chemistry and catalysis. The popularity of these ligands no doubt stems from strong NHC-metal bonds, high σ-donor character and opportunities for steric and electronic tuning. They have been applied extensively as supporting ligands in homogeneous catalysis, and in numerous cases promote higher activities than their phosphine analogues,[14-16] for example in olefin metathesis[17-21] and C–C cross-coupling reactions.[22-24]

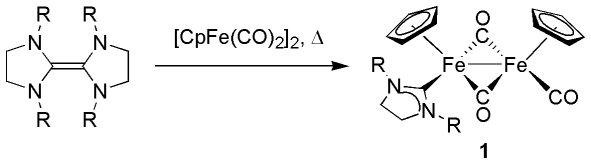
The first NHC iron complex[25] was reported just one year after Öfele[26] and Wanzlick[27,28] detailed the first NHC metal compounds in 1968. Despite this early advance, it was not until more recent years that NHC iron chemistry garnered a surge of interest. In particular, catalytic applications of NHC iron complexes are still underdeveloped when compared to the extensive and diverse exploitation of the noble metals. In this burgeoning field, C–C and C–X (X = heteroatom) bond formations and catalytic reductions have enjoyed the most progress.

An important sub-class of NHC iron compounds are those displaying a piano-stool structural motif. Typically, a cyclopentadienyl ligand or derivative provides η^5-coordination, with an NHC and two further ligands completing the coordination sphere; however the umbrella term has been extended to one- and two-legged systems and also to those bearing η^6-coordinated arene ligands. The strong NHC-metal bond renders the ligand relatively substitutionally inert, which distinguishes these complexes from classic coordination complexes bearing, for

example, phosphine ligands. In addition, the Cp ligand is typically stable towards substitution. As a result, the $[Fe(Cp)(NHC)]^+$ piano-stool motif confers—in contrast to most NHC iron complexes without a Cp ligand—fixed geometries and hence predictable substitution patterns that lead to tailoring of (re)activity.[29,30] The following section will focus on this piano-stool sub-class of NHC iron complexes. The synthetic routes towards these compounds will be described and their catalytic applications overviewed with an emphasis on reduction catalysis.

2. Synthetic Routes towards Piano-Stool NHC Iron Complexes

The first piano-stool NHC iron complex, **1**, was reported as early as 1977 by Lappert and Pye (Scheme 1).[31] Since, a diverse array of synthetic routes towards this sub-class of iron complexes has been established.[32-34] Accordingly, a broad variety of complexes with this motif have been accessed, some of which display intriguing bond activation capabilities and efficient catalytic activity. The following section summarises the diverse synthetic routes and includes representative examples.



Scheme 1. *Synthesis of bimetallic monocarbene iron piano-stool complex **1** by thermally activating NHC-dimers (R = Me, Et).[31]*

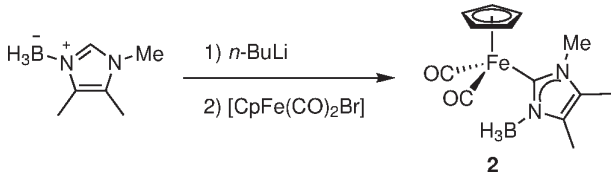
2.1. Thermal activation of enetetramines

In 1973, Lappert and co-workers pioneered the utilisation of electron rich enetetramines as precursors for the synthesis of NHC iron complexes.[35] The olefins are thermally cleaved in the presence of the $[CpFe(CO)_2]_2$ dimer to afford the bimetallic iron piano-stool complex **1** (Scheme 1).[31] This complex features an imidazolinylidene bound to one iron(I) centre and an apparent Fe−Fe interaction that is supported by two bridging carbonyl ligands. A Wanzlick equilibrium[36] between the NHC dimers (olefin) and the corresponding free carbenes has been proposed. While some studies have initially suggested a unimolecular process,[36-38] it has been shown that the formation of the equilibrium is catalysed by electrophiles.[39-43] This equilibrium is influenced by steric and electronic effects of the heterocyclic scaffold, with bulky substituents creating a bias towards the free carbene. While this route has been important

in the early years of NHC chemistry,[44] the discovery of new and more versatile routes has caused the method to become essentially obsolete.

2.2. Transmetallation

Transmetallation from intermediate NHC metal adducts is not very commonly employed for the synthesis of NHC iron complexes. Transmetallation of a base-sensitive tris(carbene)borate ligand to iron *via* deprotonation with MeMgBr and formation of the corresponding Grignard reagent has been achieved.[45] NHC lithium adducts have also been applied as transmetallating agents to iron precursors.[46] Deprotonation of a zwitterionic precursor, 3-borane-1-methylimidazole with *n*-BuLi, and subsequent reaction of the Li-adduct with an iron bromide precursor gives access to neutral complex **2** (Scheme 2).[47]



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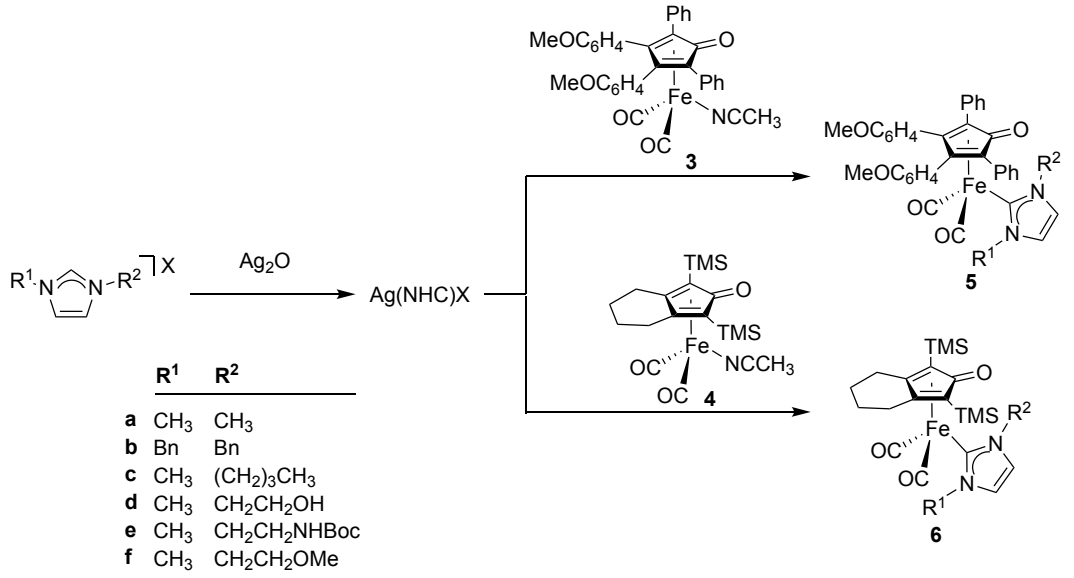
Scheme 2. *Synthesis of cyclopentadienyl 3-borane-1-methylimidazolylidene iron complex* ***2*** *using an organolithium precursor.[47]*

Silver(I) transmetallation[48] of NHC ligands is a very important and broadly applied synthetic strategy towards NHC complexes with late transition metals. However, examples of silver(I) mediated transfer of an NHC ligand to iron are rare and are usually only successful when potentially multidentate ligand precursors are employed,[49-53] or when the iron centre is in zero-valent oxidation state and electron-rich. While Cp complexes of iron(0) are scarce (*e.g.* as $Na[Fe(Cp)(CO)_2]$), Mazzoni *et al.* circumvented this issue by using a cyclopentadienone spectator ligand instead of the anionic Cp unit. They have successfully used silver carbene complexes for transmetallation to synthesise NHC iron(0) piano-stool complexes **5** and **6** (Scheme 3).[54] For this transformation, the silver carbene intermediate is first formed *in situ* by stirring the imidazolium ligand precursor in the presence of silver(I) oxide, and reacted with the solvento complexes **3** or **4** in refluxing toluene to afford the NHC iron complexes **5** or **6** respectively bearing modified neutral cyclopentadienone ligands. The authors have previously reported the formation of heterobimetallic ruthenium–silver complexes in an analogous protocol using bulky wingtip substituents.[55] Crystal data of this mixed-metal complex reveal

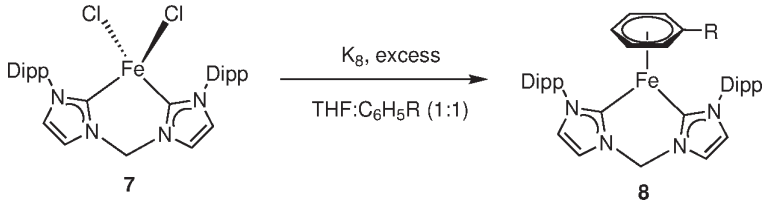
an interaction between the cyclopentadienone oxygen and the silver ion, which led to speculation that the ligand is non-innocent and facilitates transmetallation.



Scheme 3. *Synthesis of imidazolylidene iron(0) complexes with a cyclopentadienone ligand by the silver(I) transmetallation route.[54]*

2.3. Arene bonding to Fe(NHC) synthon

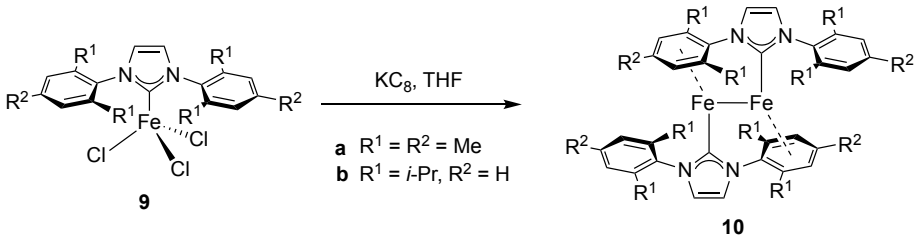
A different approach to iron(0) piano-stool complexes containing carbene ligands has been disclosed by Driess and co-workers.[56] Reduction of the tetrahedral dicarbene complex [$FeCl_2$(di-NHC)] **7** with KC_8 in the presence of PMe_3 and subsequent addition of benzene or toluene affords the two-legged piano-stool 18e$^-$ iron complex **8** (Scheme 4). The arene is rapidly replaced upon addition of CO.



Scheme 4. *Synthesis of bis-NHC η^6-arene Fe(0) complex **8** (R = H, Me; Dipp = 2,6-iPr-C_6H_3).[56]*

Similarly, the group of Ohki has demonstrated that treatment of (NHC)$FeCl_3$ complexes **9** bearing Dipp or Mes decorated NHC ligands with KC_8 affords the dinuclear Fe(0) complexes **10a,b** (Scheme 5).[57] The unusual μ-η^1(C):η^6(arene) coordination mode of the NHC ligands stabilises the Fe(0) oxidation state. The spin-state of the complexes is dependent on the wingtip

substituents. While **10a** with Mes wingtip groups adopts an S = 2 high-spin configuration, **10b** with Dipp substituents is low-spinan overall spin of S = 0. The authors speculate that the 4-methyl group of the coordinating mesityl moiety in complex **10a** forces a twisted arrangement due to its proximity to the unbound mesityl group, resulting in decreased interaction between the iron centres and inducing a high-spin state.



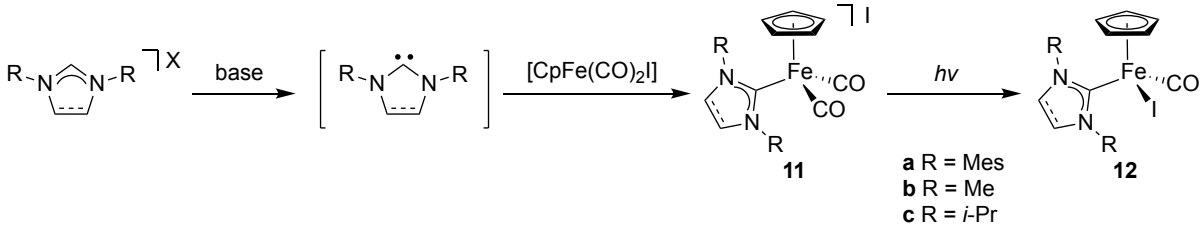
Scheme 5. *Synthesis of NHC iron(0) dinuclear complexes* ***10****.[57]*

While strictly speaking, this complex is not a member of the [Fe(Cp)(NHC)] family covered by this review, the structural similarity warrants such species to be included here. Of note, this arene bonding has only been demonstrated for benzene derivatives, and no Cp coordination to the Fe(NHC) unit has been evidenced so far. Moreover, the high lability of the arene unit in complex 8 emphasizes the benefits of the Cp ligand in imparting stability and reliable complex formation for further manipulations.

2.4. Free carbene route

The discovery of the free carbene route represents a major milestone in NHC iron chemistry. Fehlhammer *et al.* were the first to apply this methodology in 1996 with the synthesis of a hexacarbene iron complex.[58] Since this report, generation of the free carbene with an appropriate base and subsequent NHC coordination has been the preferred route to prepare NHC iron complexes.[32-34] Potassium bases are generally favoured over lithium analogues in order to avoid potentially stable alkali metal-carbene adducts.[43,59,60] Surprisingly, it has taken some years for this synthetic approach to be applied to the synthesis of piano-stool iron complexes. The first example appeared in 2003, when Guerchais and co-workers[61] reported

the synthesis of complex **11** via an *in situ* generated free carbene and subsequent metallation with [CpFe(CO)$_2$I] as metal precursor (Scheme 6).



Scheme 6. *Synthesis of imidazolylidene and imidazolinylidene iron piano stool complexes **11** and **12** using the free carbene route.[61,62]*

The dicarbonyl complexes **11** are smoothly converted to the corresponding neutral compounds **12** upon photoinduced cleavage of one Fe–CO bond and coordination of iodide. Following this report, our group[62-66] and others have expanded the scope of this synthesis by varying the wingtip substituents,[67,68] heterocyclic framework,[66,69-71] co-ligands[71] and installing chelating groups to form dicarbene,[72] picolyl-carbene,[62] and pyridine-carbene complexes.[64] We have further demonstrated that bimetallic complexes can be accessed using dicarbene ligands with either flexible (**13**) or rigid (**14**, **15**) linkers (Figure 1).[63-65] When a methylene group links the two carbenes (as in **13**), it is necessary to perform the reaction at low ligand concentrations to avoid a chelating mononuclear complex. Diastereomers of **13** and **14** are formed as a result of the stereogenic iron centre.

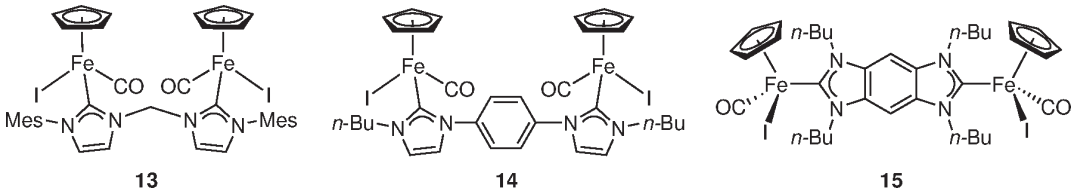
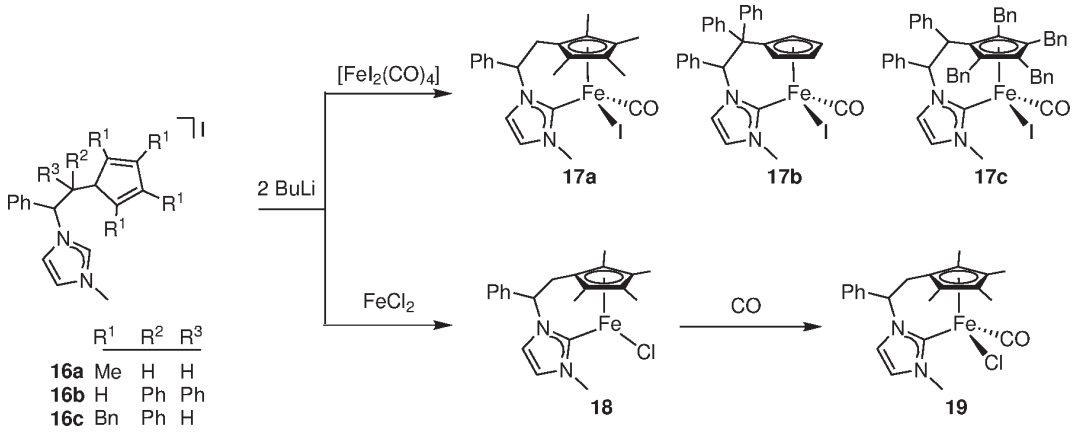


Figure 1. *Bimetallic piano stool complexes **13–15** synthesised by the free carbene route.[63,64]*

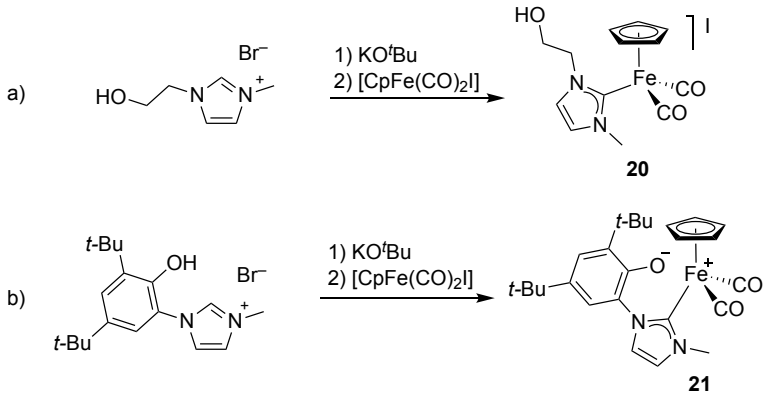
Cyclopentadienyl-functionalised NHC iron complexes **17** and **18** have also been prepared by this route (Scheme 7).[73] The bifunctional ligand precursor **16** is deprotonated by two equivalents of *n*-BuLi to afford simultaneously the free carbene and the anionic cyclopentadienyl, which is metallated using [FeI$_2$(CO)$_4$] or FeCl$_2$. This protocol results in the formation of coordinatively saturated (**17**) or unsaturated (**18**) complexes respectively. Sixteen-

electron complex **18** is smoothly converted to the air-stable 18e⁻ species **19** when exposed to a CO atmosphere.



Scheme 7. *Preparation of chelating cyclopentadienyl-NHC complexes* ***17–19*** *by the free carbene route.[73]*

Recently the free carbene route has been applied to NHCs comprising pendant hydroxyl and phenol groups (Scheme 8).[74] The hydroxyl-NHC ligand is metallated using one equivalent of KO^{t}Bu and [CpFe(CO)$_2$I], resulting in a cationic dicarbonyl complex where the hydroxyl group is not included in the coordination sphere (Scheme 8a). One equivalent of base is insufficient to cleanly metallate the phenol substituted ligand. When two equivalents of KO^{t}Bu are used, a zwitterionic dicarbonyl complex is obtained with a cationic iron centre and a pendant phenoxide anion (Scheme 8b).



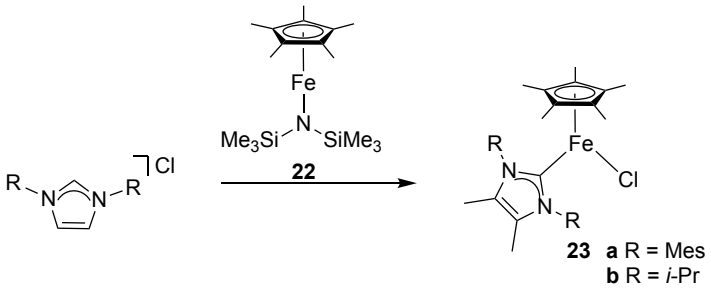
Scheme 8. *Synthesis of cationic hydroxyl complex* ***20*** *and the zwitterionic phenoxide complex* ***21****.[74]*

While the free carbene route is relatively versatile, the sensitivity of many functional groups to basic conditions imposes some restrictions. Another limitation is the stability of some of the free carbenes, especially when small (*e.g.* methyl) groups are bound to the heterocyclic

nitrogen atoms. Such instability has been highlighted by Bertrand and coworkers, who have disclosed the degradation of certain imidazol-5-ylidenes and 1,2,3-triazolylidenes due to rearrangement.[59,75,76]

2.5. Internal base (aminolysis) route

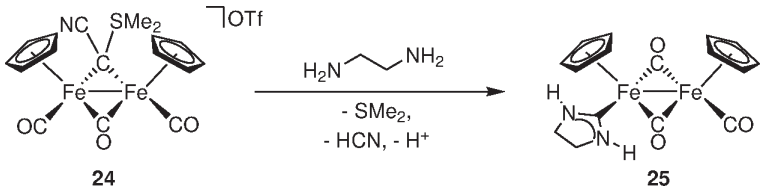
Danopoulos and co-workers[77] first demonstrated the synthesis of NHC iron complexes through direct reaction with the internal base contained in the $Fe[N(SiMe_3)_2]_2$[78] precursor. In recent years, this method has become highly popular[79] since it tends to be cleaner and higher yielding than the classic free carbene route. Using the Cp-modified precursor **22**,[80] coordinatively unsaturated iron piano-stool complexes **23** can be accessed (Scheme 9).[81] Preparation and use of these amide precursors requires rigorously inert conditions due to their high moisture sensitivity. Typically they have to be freshly prepared before each use, which is a drawback when considering this route.



Scheme 9. *Synthesis of 2-legged 16 electron piano-stool complexes* ***23*** *using the 'internal base' method.[81]*

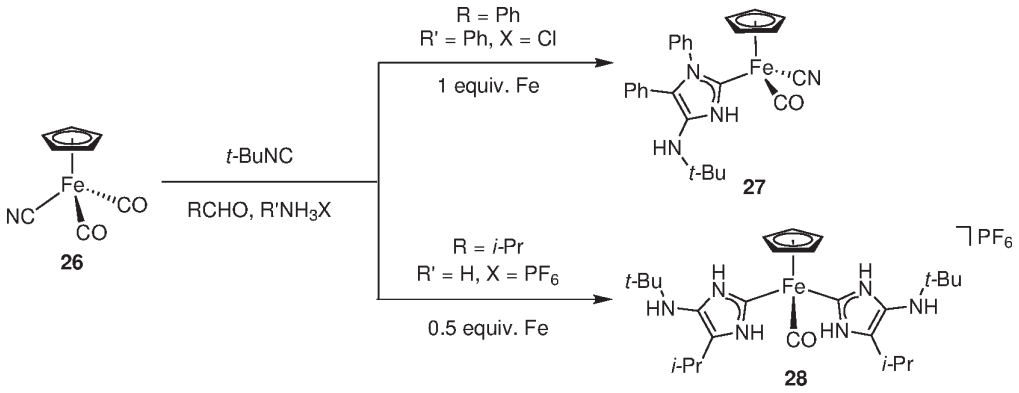
2.6. NHC formation within the iron coordination sphere

Many of the early piano-stool NHC iron complexes have been synthesised *via* nucleophilic substitution reactions onto coordinated ligands, thereby forming the carbene directly on the iron centre without the need to prepare ligand precursors. Angelici has pioneered this route and has prepared monometallic piano-stool complexes by treating the thiocarbonyl or dithiocarbene complexes, $[CpFe(CO)(CS)SnPh_3]$ and $[CpFe(CO)_2(C(SMe)_2)]PF_6$ respectively, with ethylenediamine.[82,83] Later, Albano and Busetto[84,85] have used a similar approach to prepare a bimetallic complex which extends the class previously established by Lappert and Pye (Scheme 1).[31] Ethylenediamine is reacted with a dimeric sulfonium salt **24** to afford bimetallic complex **25** bearing one imidazolinylidene ligand (Scheme 10).



Scheme 10. *Preparation of dimeric NHC iron complex* ***25*** *starting from a sulfonium salt precursor.[91-85]*

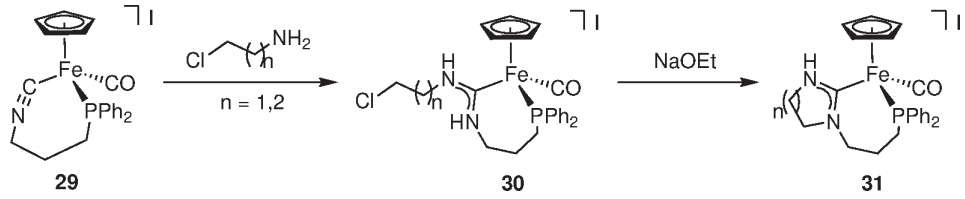
Fehlhammer *et al*. have expanded this method towards monometallic complexes starting from (iso)cyanide metal precursors.[86,87] Their approach is based on treament of the benzonitrile complex $[CpFe(CNPh)(CO)_2]PF_6$ with aziridine and tetrabutylammonium bromide.[86] As an extension of this approach, multicomponent reactions starting from cyanide complex **26**, an aldehyde, an isocyanide and an ammonium or anilinium salt affords piano-stool NHC iron complexes (Scheme 11).[87] Both monocarbene (**27**) and biscarbene (**28**) complexes are accessible as a result of the two available cyanide ligands. The stoichiometry of the reaction and the nature of the components determine the number of carbenes formed at the iron centre. For example, using half an equivalent of **26** in the presence of benzaldehyde, *t*-butyl isocyanide and aniline hydrochloride affords complex **27** exclusively.



Scheme 11. *Multicomponent synthesis of mono- and biscarbene piano-stool complexes* ***27*** *and* ***28****.[87]*

Starting from a phosphine substituted isocyanide complex **29**, *C*,*P*-chelating NHC complexes **31** have been prepared (Scheme 12).[88] The synthesis is adapted from a protocol towards acyclic diamino-carbene ligands developed much earlier.[89] Initial coordination of the diphenylphosphine substituted isocyanide results in a *C*,*P*-chelating complex **29**. Treatment of this complex with either 2-chloroethylamine or 3-chloropropylamine gives access to complexes **30**, pre-organised towards formation of the five- or six-membered heterocyclic

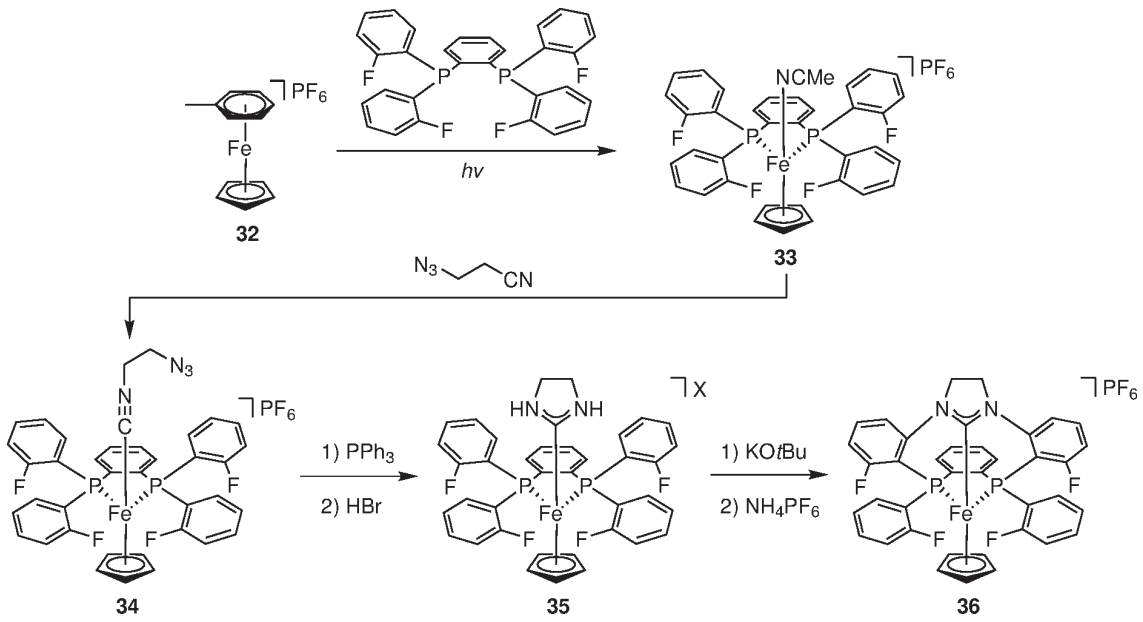
carbene, respectively. Dehalogenation and ring closure is induced by sodium ethoxide to afford the NHC complexes **31**.



Scheme 12. *Synthesis of the C,P-chelating imidazolinylidene iron complex **31**.[88]*

2.7. Templated synthesis

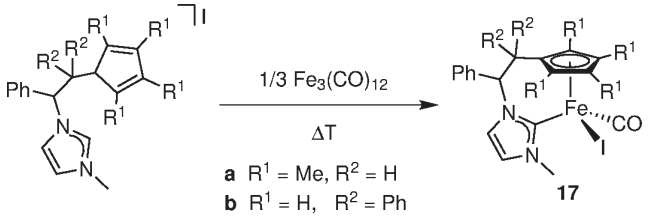
In 2010, Hahn *et al.* reported the templated synthesis of a non-classical NHC piano-stool iron complex **36** with a tridentate [11]ane-P_2C^{NHC} ligand (Scheme 13).[90] The novel, four step synthesis is initiated by coordination of the diphosphane 1,2-bis[bis(2-fluoro-phenyl)phosphanyl]benzene to the cationic Cp/toluene iron(II) precursor **32** to give complex **33**. Substitution of the coordinated MeCN ligand by 2-azidoethyl isocyanide yields intermediate **34**. An intramolecular Staudinger reaction involving the pendant azide of the isocyanide ligand results in the formation of a protic NH,NH imidazolinylidene ligand (**35**). Deprotonation of the N−H moieties with KO^{t}Bu induces a ring closure reaction between the pre-organised ligands and affords complex **36**.



Scheme 13. *Templated ring-closure synthesis of the piano-stool iron complex* ***36*** *containing a P,C,P-chelating imidazolinylidene.[90]*

2.8. Direct synthesis

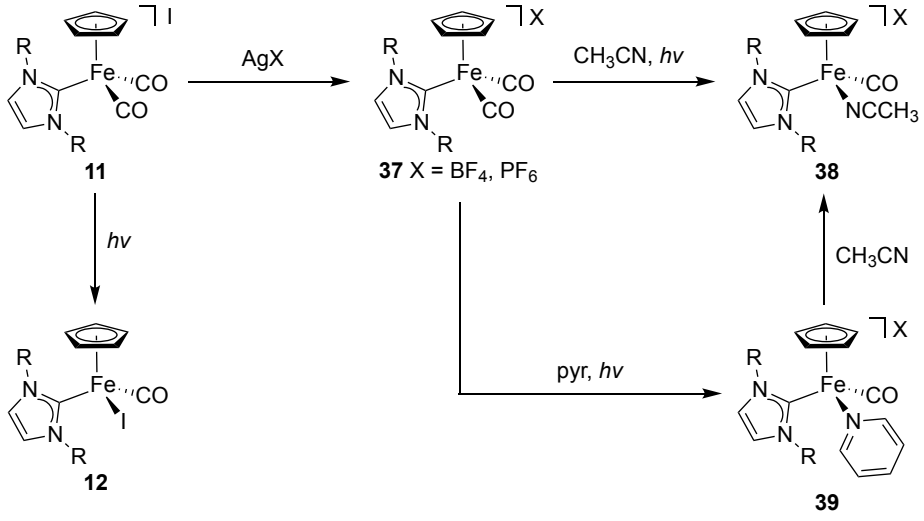
Royo *et al*. have discovered a direct synthesis of iron(II) cyclopentadienyl-tethered imidazolylidene complexes **17** by refluxing the iron(0) trimer $Fe_3(CO)_{12}$ and a cyclopentadiene-functionalised imidazolium salt precursor in toluene (Scheme 14).[91,92] The authors have speculated that this reaction involves an initial oxidative addition of the imidazolium C–H bond to the iron(0) centre, followed by elimination of the iron-bound hydride and the cyclopentadienyl proton to afford the iron(II) complex. This mechanism is supported by earlier work using related ruthenium precursors. For example, direct metallation of indenyl-[93] and cyclopentadienyl-functionalised[94] imidazolium ligand precursors with $Ru_3(CO)_{12}$ has also been proposed to proceed *via* a metal-hydride species. Detection of any metal hydride species in this metallation process has been precluded so far, presumably because of the high reactivity of this intermediate.



Scheme 14. *Direct synthesis of the cyclopentadienyl-tethered imidazolylidene Fe(II) complexes* ***17a,b****.[91,92]*

3. Reactivity of Piano-Stool NHC Iron Complexes

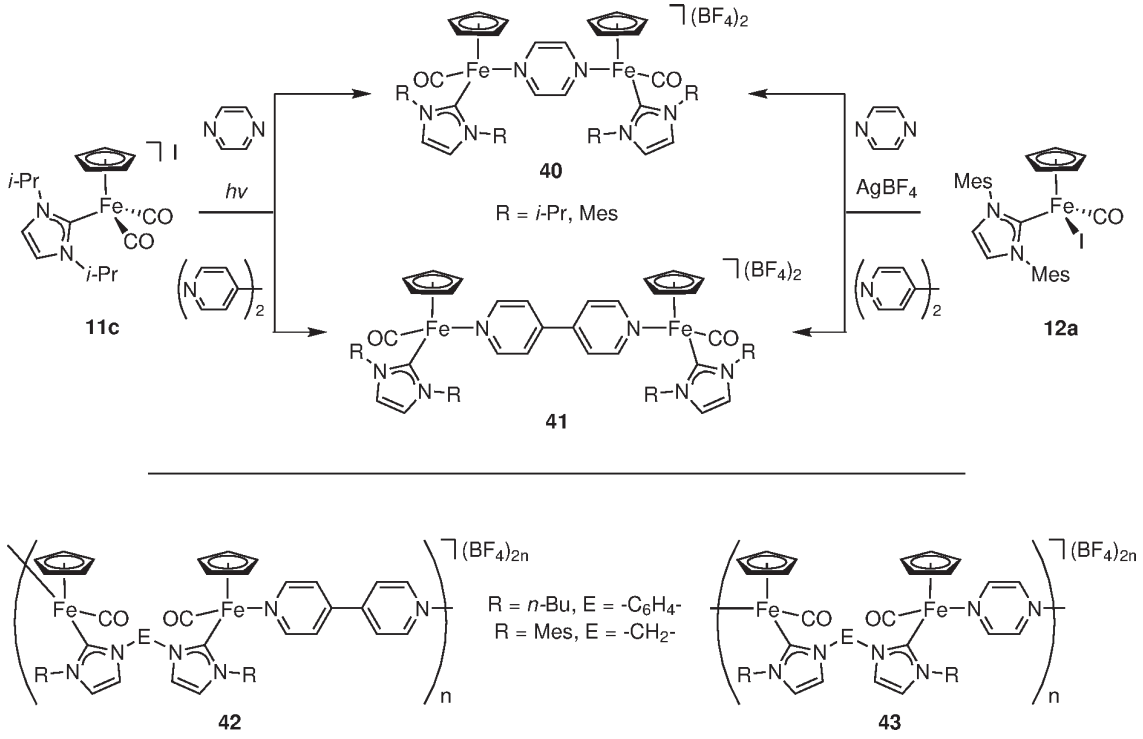
Reactivity studies have elucidated the rich potential of this class of NHC iron complexes, both in the area of catalysis[32-34] and also towards electronically active materials.[63,95] Guerchais *et al.* first described the facile exchange of one carbonyl ligand for iodide (**12**) or acetonitrile (**38**) under UV irradiation (Scheme 15).[61] The authors noted that attempts to exchange the second carbonyl ligand under the same conditions did not proceed. In contrast, analogous phosphine complexes lost both carbonyl ligands. This difference has led the authors to speculate that the strong σ-donation of the NHC ligands increases π-back-bonding to CO, and reduces its lability. In support of this conclusion, Özdemir has reported benzyl-substituted imidazolinylidene systems which donate more electron density than IMes, and which render both carbonyl ligands resistent to dissociation.[68] We have reported the exchange of a carbonyl ligand for pyridine to form complex **39** using a similar protol to Guerchais.[63] This ligand is quite labile, as acetonitrile very readily replaces pyridine in the coordination sphere to generate complex **38**.



Scheme 15. *Typical reactivity patterns of piano-stool dicarbonyl NHC iron complexes (R = i-Pr, Mes).[61,63]*

We have exploited the selective substitution of one carbonyl ligand to prepare novel bi- and polymetallic systems. Reaction of monomeric imidazolylidene complexes with pyrazine or 4,4'-bipyridine yields bimetallic complexes **40** and **41** (Scheme 16).[63] Two different methodologies have been employed depending on the wingtip substituents. In the case of the

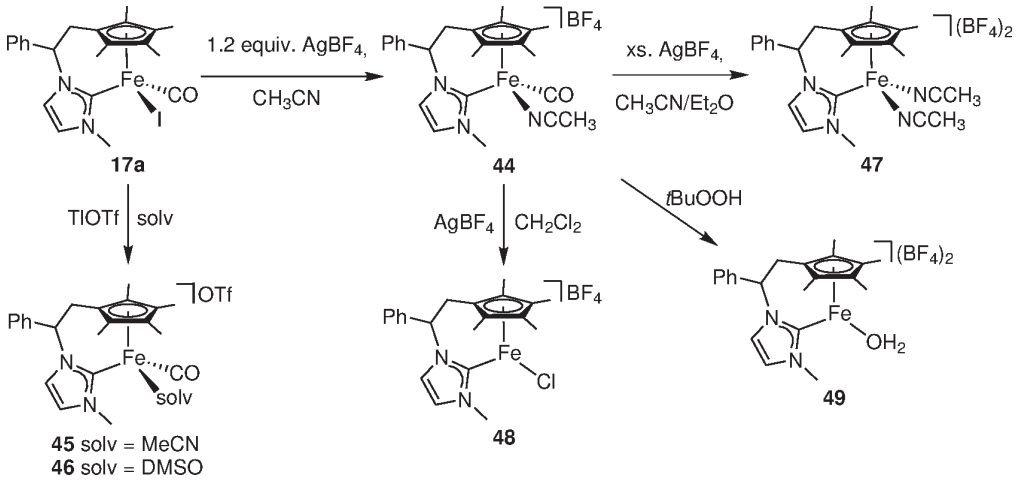
*i*Pr substituents, UV-irradiation of the cationic dicarbonyl species **11c** in the presence of the relevant heterocyle affords dimeric compounds. This route fails when starting from the analogous IMes complex **11a**. Therefore an alternative method has developed starting from the neutral complex **12c** and abstracting the iodide with $AgBF_4$ to allow diimine coordination. Electronic coupling between the iron centres is observed by cyclic voltammetry when a pyrazine linker is employed, but is absent in the bipyridine-bridged complexes. The dimers have poor stability in solution at room temperature. This methodology has been expanded by combining dicarbene bridged bimetallic complexes **13** and **14** with diimine ligands as synthons for the preparation of main-chain organometallic co-polymers **42** and **43** (Scheme 16).[63] These polymeric compounds demonstrate a surprising higher stability compared to the bimetallic diimine bridged complexes **40** and **41**.



Scheme 16. *Synthesis of bimetallic complexes and main-chain organometallic polymers containing redox-active iron(II) centres.[63]*

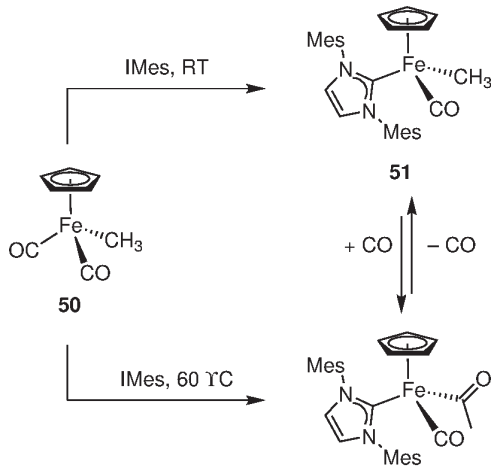
Cyclopentadienyl-tethered-NHC complexes are amenable to various ligand exchange and oxidation reactions (Scheme 17).[96] Depending on the equivalents of $AgBF_4$ and the solvent conditions applied, different complexes are accessible from the neutral iodide complex **17a**. With close to stoichiometric equivalents of the silver salt, the cationic mono-acetonitrile Fe(II) complex **44** is obtained. When exposed to an excess of $AgBF_4$ in CH_3CN/Et_2O, the iron centre

is oxidised to a dicationic bis-acetonitrile iron(III) complex **47**. In CH_2Cl_2 solution, a slight excess of $AgBF_4$ once again results in oxidation to Fe(III) and loss of CO, producing the unsaturated chloride complex **48** where the chloride has presumably been abstracted from the solvent. Treatment of complex **17a** with TlOTf eliminates the potential for iron oxidation, and allows for the smooth preparation of mono-acetonitrile and dimethylsulfoxide cationic Fe(II) complexes **45** and **46** in the presence of the relevant solvent. Treatment of **44** with *t*BuOOH has been proposed to afford the 16e$^-$ Fe(III) aqua complex **49**. ^{57}Fe Mössbauer spectroscopy confirmed an Fe(III) species and elemental analysis supported the proposed structure, however full characterisation has been precluded by the low solubility of the compound.



Scheme 17. *Ligand exchange and oxidation reactions of the Cp*-tethered NHC iron complex* ***17a****.[96]*

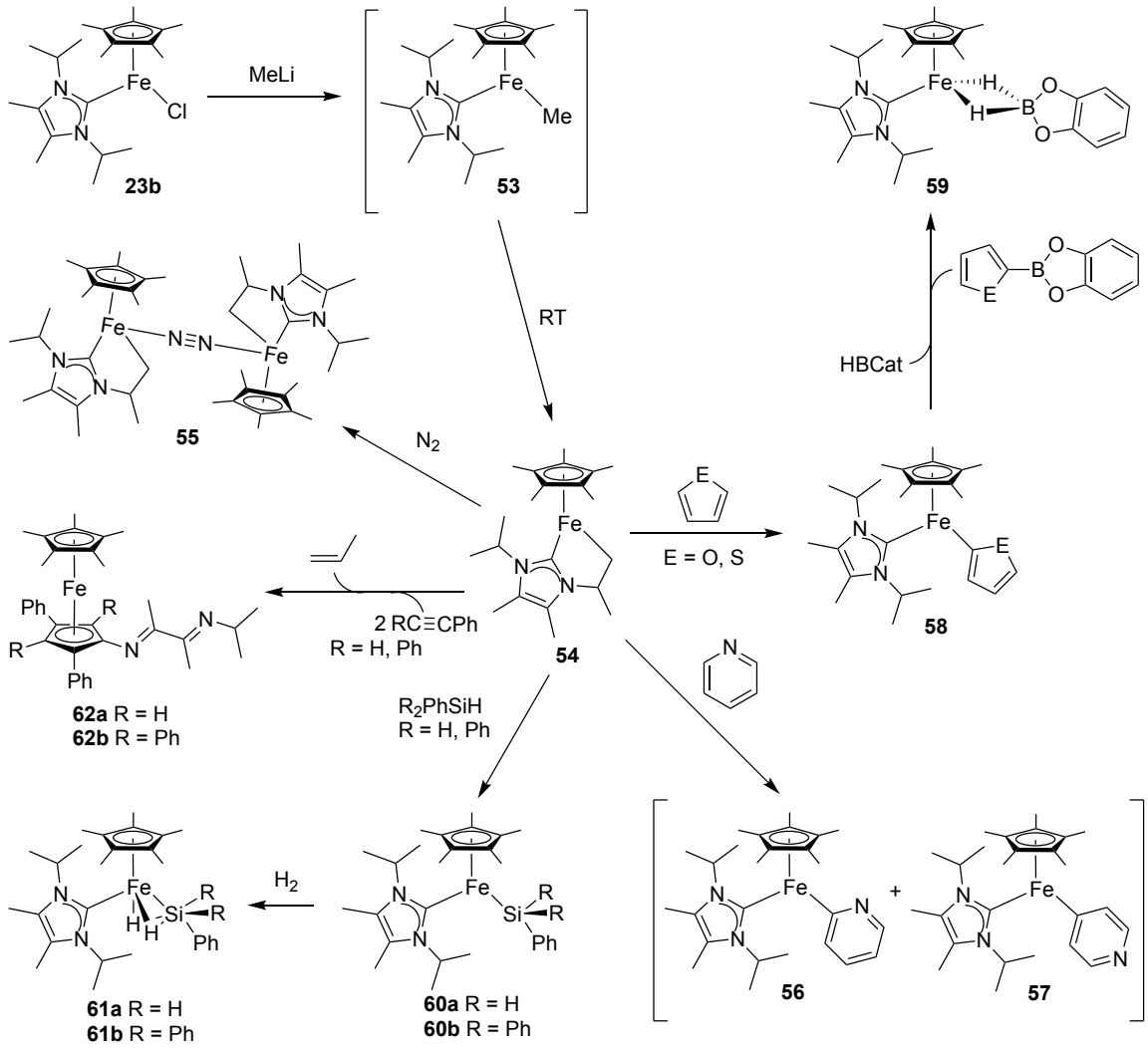
Reversible carbonylation of alkyl iron-NHC piano-stool complexes has been demonstrated (Scheme 16).[71] Starting from the dicarbonyl methyl complex **50**, coordination of IMes proceeds at room temperature to afford complex **51** containing a methyl ligand. When the synthesis is carried out at elevated temperatures, the migratory insertion of a carbonyl ligand into the Fe–Me bond (**52**) is observed. Gradual decarbonylation of **52** to **51** occurs when the complex is stored in solution. Complex **52** is slowly regenerated under a CO atmosphere of 1.5 atm, and faster if the CO pressure is increased to 5 atm.



Scheme 18. *Reversible migratory insertion of CO into Fe–Me bond of the alkyl iron complex* ***50****.[71]*

Coordinatively unsaturated 16e$^-$ complexes are very efficient at C–H bond activation.[81] The first indication of this reactivity stems from treatment of the IMes complex **23a** (*cf.* Scheme 9) with methyl- or phenyllithium. While the complexes are stable in solution at room temperature, heating to 60 °C for several days induces an intramolecular C–H bond activation and cyclometallation occurs involving an *ortho*-methyl group of the mesityl wingtip group with concomitant release of methane or benzene. In contrast, when the *i*-Pr complex **23b** is treated with MeLi (Scheme 19), the alkyl complex **53** is not sufficiently stable for isolation as a result of the lower thermal stability, which accelerates intramolecular C–H bond activation at room temperature to give complex **54**. Evidence for the transient complex **53** has been obtained by addition of a CO ligand and isolation of the resulting saturated 18e$^-$ carbonyl complex. The lower stability of **53** compared to the dimesityl complex has been attributed to the decreased steric demand of the *i*-Pr groups. The cyclometallated complex **54** is highly reactive due to its coordinative unsaturation, and it reacts even with molecular nitrogen to form the N_2-bridged dimer **55**. The activated and cyclometallated IPr complex **54** demonstrates remarkable reactivity with thiophenes, furans, and pyridine and affords the products of C–H bond activation (16e$^-$ complexes **56**–**58**) rather than heteroatom coordination to form the corresponding coordinatively saturated 18e$^-$ complexes. Presumably, a σ-bond metathesis reaction occurs during C–H activation whereby the iron-bound methylene group deprotonates the heteroarenes. The selectivity of C–H bond activation has been suggested to arise due to an interaction between the heteroatom and the iron centre. H/D exchange experiments have revealed that the 2- and 4-position of pyridine are reversibly activated. Only complex **57** from C4–H bond activation is arrested upon reaction with *tert*-butylisocyanide or CO and isolation

of the more stable $18e^-$ complex. Activated thiophenes and furans are regioselectively borylated in the presence of stoichiometric amounts of catecholborane (HBcat). The transformation is not catalytic due to the high thermal stability of the formed borohydride complex **59**, which is unreactive with the substrates. Catalytic borylation of heteroarenes has, however, been achieved later with a similar catalytic system (see section 5.1).[97]

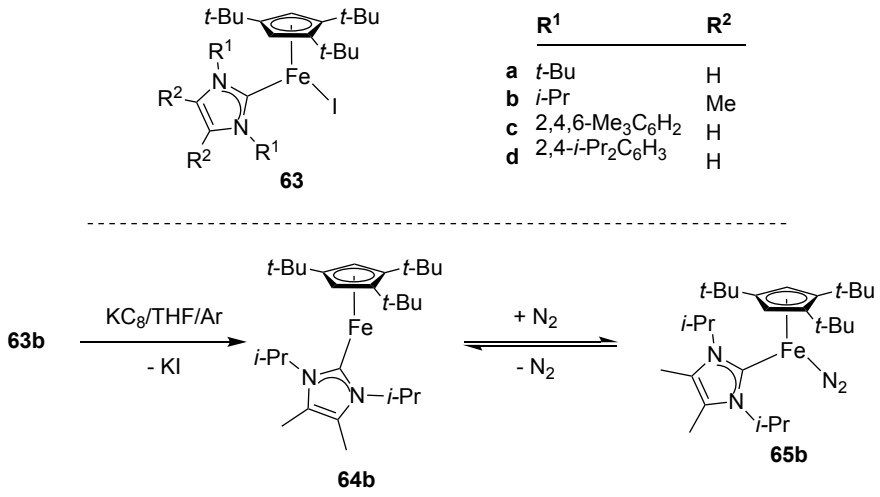


Scheme 19. *Formation and reactivity scheme of the coordinatively unsaturated piano-stool iron complex **54**.*[81,97-99]

Furthermore, facile and reversible Si–H bond activation is accomplished upon treatment of the cyclometallated complex **54** with hydrosilanes.[92] When the silyl complex **60** is treated with molecular hydrogen, the iron(IV) dihydride species **61** is formed. Exposing the cyclometallated complex **54** to alkynes results in ring-opening of the NHC ligand and formation of a diimine substituted η^5-cyclopentadienyl complex **62**, in which two alkyne equivalents are

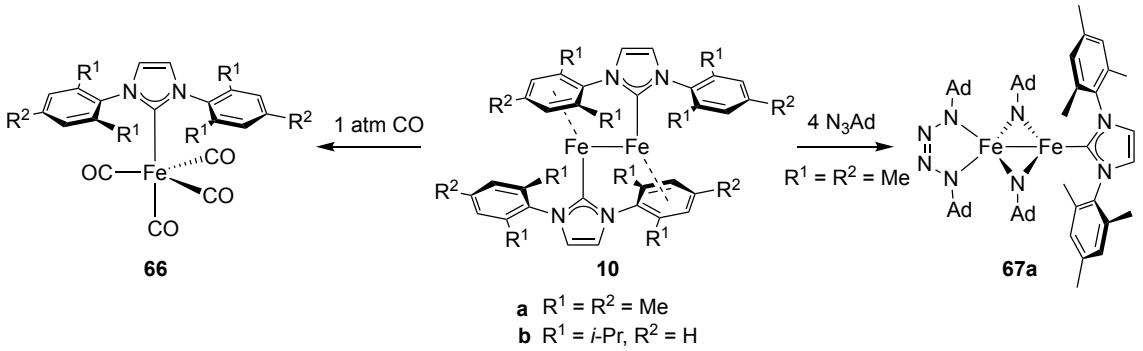
incorporated.[99] During this transformation, an intramolecular C–N bond activation occurs with concomittant loss of an *iso*-propyl wingtip group as propylene.

The unsaturated 16e$^-$ complexes **63** bearing a Cp' ligand (Cp' = η^5-1,2,4-(*t*Bu)$_3$C$_5$H$_2$) analogous to complex **23b** have been prepared by Walter *et al.* (Scheme 20).[100,101] These complexes adopt a high-spin configuration (S = 2) in contrast to the putative intermediate-spin (S = 1) of their Cp* equivalents. The authors speculate that the decreased ligand field strength and greater steric demand of the Cp' ligand *vs.* Cp* creates a bias towards longer bond lengths and thus a high-spin Fe(II) centre. Reduction of complex **63b** with KC_8 affords the one-legged piano-stool 15e$^-$ complex **64b**. This high-spin complex (S = 3/2) reversibly binds N_2. To yield complex **65b**, a process that is accompanied by a spin-state change to the low-spin (S = ½ for 17e$^-$ species **65b**) and a change in colour from bright to olive green.



Scheme 20. *Reversible dinitrogen bonding to a one-legged piano-stool 15e$^-$ complex.[100,101]*

The iron(0) dinuclear complexes **10a,b** (*cf* Scheme 5) provide access to zero-valent iron carbonyl species of the form (NHC)Fe(CO)$_4$ (**66**, Scheme 21) upon exposure to 1 atm of CO.[57] This is an alternative to previously established methods using the free carbene route and $Fe_3(CO)_{12}$ [99] or $Fe(CO)_5$ [102] precursors. Furthermore, the dimeric complex **10a** reacts with 4 equivalents of 1-azidoadamantane to afford the iron-imido complex **67a**. It is proposed that a di-imido-bridged dinuclear complex initially forms, followed by dissociation of an IMes ligand and formation of an Fe=NAd bond (Ad = adamantyl). A final equivalent of AdN_3 is suggested to then undergo a [3+2] cycloaddition with the Fe=NAd unit to form the tetrazene moiety and finally complex **67a**. Both these reation trajectories emphasize the substantially higher lability of the Fe-arene bond in comparison to the Fe–Cp bond.



Scheme 21. *Reactivity of the dinuclear Fe(0) complexes* ***10****.[57]*

4. Reductions Catalysed by Piano-Stool NHC Iron Complexes

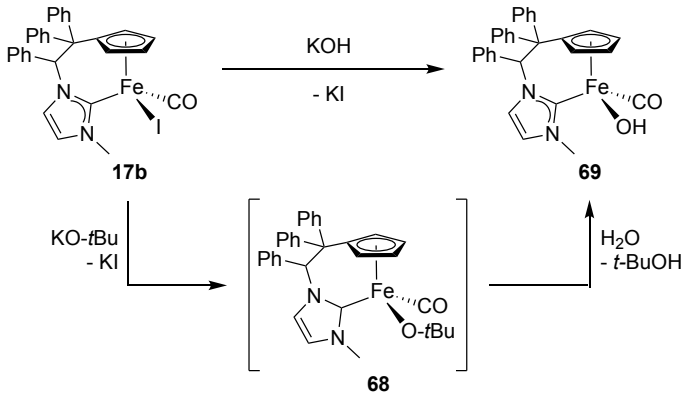
The reduction of unsaturated functional groups such as olefins and carbonyls are essential transformations in organic chemistry. Hydrogenation, transfer hydrogenation, and hydrosilylation processes catalysed by late transition metals such as Rh, Ir, Ru, Pd and Pt still dominate the field of catalytic reductions. However, iron complexes are gradually emerging as competitive systems, illustrated by Chirik's Fe NNN pincer compounds, which reach higher turnover frequencies (TOFs) in direct hydrogenation than Crabtree's and Wilkinson's catalyst,[103], and by Morris' Fe PNNP system for highly efficient asymmetric transfer hydrogenation catalysis.[104] NHC iron complexes have been predominantly applied as hydrosilylation catalysts, however some hydrogenation[105] and transfer hydrogenation[73,79,106] activity has also been noted.

4.1. Hydrosilylation

Hydrosilylation is a popular strategy since it can be operated under relatively mild conditions compared to other reduction methods. Safety considerations also make it an attractive choice, since it avoids using flammable H_2 gas, instead employing non-toxic hydrosilanes as reducing agents. In 2010, Royo *et al*. reported the first set of NHC iron hydrosilylation catalysts.[73] The coordinatively unsaturated Cp*-tethered imidazolylidene iron complex **18** (*cf* Scheme 7) efficiently converts substituted benzaldehydes to their corresponding silyl ethers at 1 mol% catalyst loading. A range of electron-withdrawing groups are tolerated in the substrate including nitro, cyano, and bromo substituents. Under these conditions, ketones and aliphatic

aldehydes are not reduced. While the saturated iodide complexes **17** are inactive for the hydrosilylation of ketones, the related acetonitrile complex **44** (*cf* Scheme 17) reduces acetophenone quantitatively within 5 hours with 0.5 mol% catalyst loading.[96]

Additives substantially modify the activity of the virtually inactive complex **17**.[107] In particular, catalytic quantities of KO^{t}Bu lead to significantly enhanced conversion of ketone substrates. Attractively, quantitative conversions have been achieved using the inexpensive polymeric silane PHMS. In contrast, activation of complex **17b** with catalytic amounts of $AgBF_4$ rather than KO^{t}Bu promotes the efficient reduction of sulfoxides.[99] A stoichiometric reaction of the precatalyst with *tert*-butoxide has been carried out to determine the identity of the active catalyst. This reaction affords a hydroxide complex **69** in lieu of the expected alkoxide compound **68** (Scheme 22).[107] The authors have suggested that traces of water in the deuterated solvent hydrolyse the proposed alkoxide intermediate. To confirm its structure, the hydroxide complex **69** has also been prepared by reaction of **17b** with an excess of KOH.



Scheme 22. *Generation of the iron hydroxide species* ***69****.[107]*

The well-defined neutral and cationic IMes piano-stool complexes **11** and **12** first described by Guerchais[69] (see Scheme 5) are also active hydrosilylation catalysts.[108-110] Visible light irradiation is essential for the activation of the cationic complex, while the neutral complex requires no activation and reduce aldehydes at mild temperatures (RT). However, the neutral complex does not catalyse the hydrosilylation of ketones such as acetophenone, even under harsh reaction conditions (toluene, 100 °C). In contrast, the dicarbonyl catalyst precursor is highly versatile and efficiently converts aldehydes and ketones.[108] Upon increasing catalyst loadings from typically 1 mol% to 5 mol%, also imines,[109] and secondary and tertiary amides[110] are converted to their corresponding amines. Primary amides are converted to nitriles under the same conditions (see below). Analogous cationic complexes bearing

imidazolinylidenes,[68] and benzimidazolylidenes[69] have also been evaluated as catalysts for aldehyde and ketone hydrosilylation and show comparable activity to the IMes complex. Recently, we have shown that the triazolylidene ligand also supports the efficient hydrosilylation of benzaldehyde and acetophenone derivatives with high turnover frequencies of up to14,400 h^{-1}.[66] Several features of the reaction, including inhibition of the catalysis by radical scavengers, support a mechanism involving single-electron transfer processes and the formation of persistent radicals. Anionic NHCs bearing an imidate (*imid*NHC, **70** and **71**, Figure 2) or malonate (**72-74**, *malo*NHC) backbone have been investigated as zwitterionic complexes (**70**, **72** and **73**) or, after post-modification with MeOTf, as cationic complexes (**71** and **74**).[70] The more electron-donating anionic *malo*NHCs induce higher activities than the neutral methylated ligands, while the imidate modifications result in generally poorer conversions. These activity data indicate that the iron centre is more active in hydrosilylation when coordinated to strongly donating carbenes such as triazolylidenes and anionic *malo*NHCs.

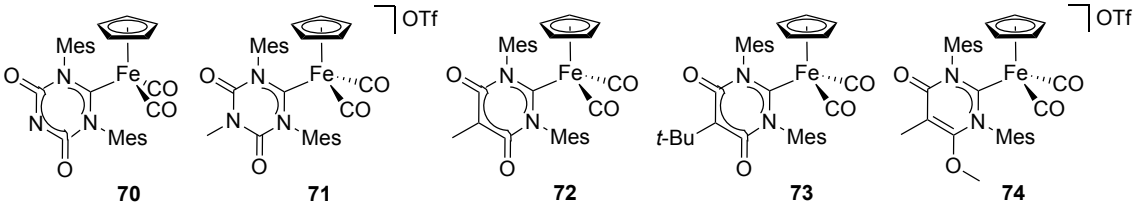
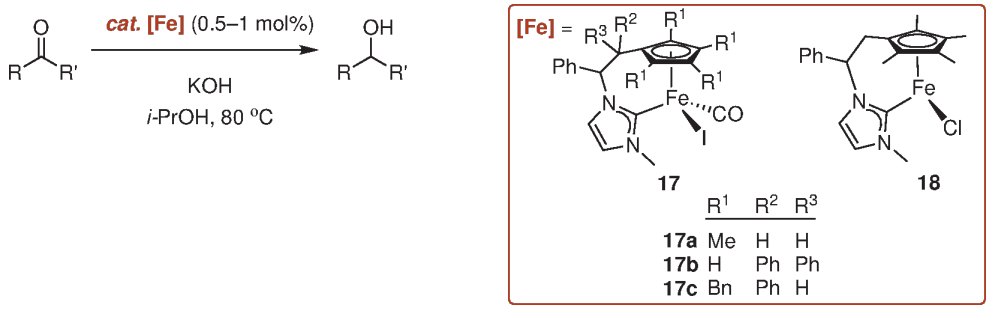


Figure 2. *Zwitterionic and cationic maloNHC and imidNHC complexes* ***70-74****.[70]*

4.2. Transfer hydrogenation

Transition metal-catalysed transfer hydrogenation (TH) is currently one of the most popular protocols towards carbonyl reduction.[111] In this process, the catalyst abstracts a hydride and a proton from an appropriate donor and delivers them to the carbonyl substrate. Typical hydrogen donors are basic *iso*-propanol or a formic acid/triethylamine system, although other alcohols (such as ethanol and glycerol) have also been employed. The well defined Cp- and Cp*-tethered NHC iron complexes **17** and **18** are active catalysts for the TH of ketones using *i*-PrOH as hydrogen source (Scheme 23).[73]



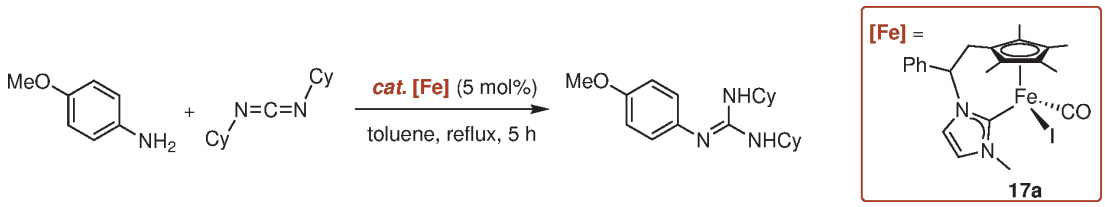
Scheme 23. *Transfer hydrogenation of ketones catalysed by Cp- and Cp*-tethered NHC iron complexes* ***17*** *and* ***18****.[73]*

All complexes reduce acetophenone in good yields at 1 mol% catalyst loading. The catalytic performance is insensitive to cyclopentadienyl substitution and also to changes in the co-ligands as there has been little variation in activity between complexes **17a–c** and **18**. A series of cationic dialkyl-substituted imidazolylidene dicarbonyl iron complexes reduce cyclohexanone with turnover numbers (TONs) up to 200.[112] When the catalysts are generated *in situ*, conversions are slightly lower than those for the isolated complexes. There is no clear correlation between the nature of the wingtip substitution and the observed catalytic activity, however it has been noted empirically that performance is generally higher when the NHC contains identical rather than different wingtip substitutents.

5. Other Catalytic Applications

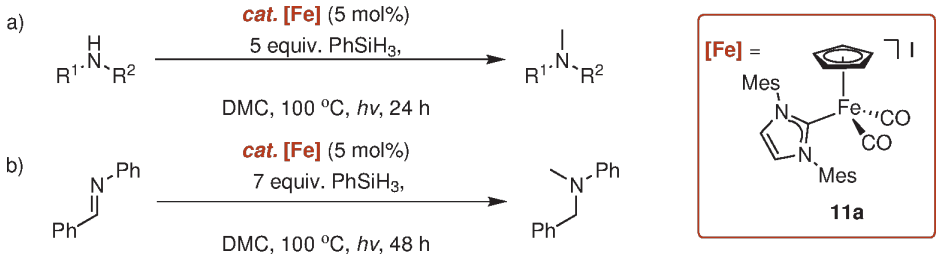
5.1. C–X bond formation

Royo has reported the first example of iron-catalysed guanylation of amines (Scheme 24).[113] With the Cp*-tethered imidazolylidene iron complex **17a** (5 mol%; see Scheme 7), quantitative yields of the guanidine product are obtained from *p*-anisidine and N,N'-dicyclohexylcarbodiimide (DCC) as substrates in refluxing toluene within 5 h. While this activity is promising, the simple $Fe(OAc)_2$ salt is substantially more active, reaching full conversions after 2 h under the same conditions and tolerating low catalyst loadings of just 2 mol%.



Scheme 24. *Guanylation of p-anisidine with DCC catalysed by iron complex* ***17a****.[113]*

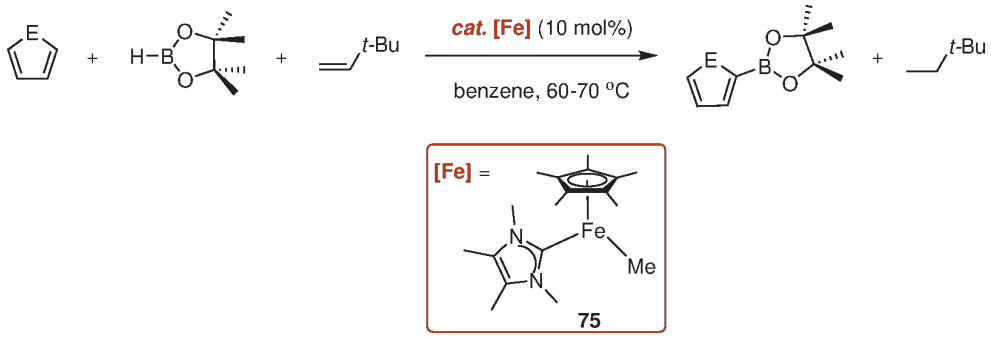
The catalytic scope of the cationic piano-stool complex **11a** (Scheme 6) has been further expanded by application in the methylation of secondary amines using dialkylcarbonates and hydrosilanes (Scheme 25a).[114] Dialkylcarbonates represent a less toxic alternative to classic methylating agents such as methyl halides/triflates or dimethylsulfide. N-alkylaniline derivatives are converted in good to excellent yields with dimethylcarbonate (100 °C, 24 h) with unsubstituted anilines, or anilines with electron-donating substituents. Longer reaction times of up to 48 h are required when electron-withdrawing *para*-substituents are present. Diphenyl, dibenzyl and dialkyl substituents require more forcing conditions of 120 °C, using higher boiling diethylcarbonate, and give only moderate conversion even after 48 h. A one pot reduction-methylation (Scheme 25b) of imines has been achieved using 7 equivalents of $PhSiH_3$. Interestingly, a methyl group is delivered also when diethylcarbonate instead of DMC is used, indicating that the carbonyl carbon acts as the C_1 source. This observation together with complementary work on the ruthenium-catalysed methylation of amines with CO_2 [115] suggests the formation of an urea intermediate. Indeed, a control experiment under catalytic conditions in the absence of dimethylcarbonate has demonstrated that N,N'-dimethyl-N,N'-diphenylurea is quantitatively converted to N,N-dimethylaniline with **11a**, along with N-methylaniline as a by-product.



Scheme 25. *a) Methylation of secondary amines and b) reduction-methylation of imines with dimethylcarbonate (DMC) catalysed by the piano-stool NHC iron complex* ***11a****.[113]*

The coordinatively unsaturated complex **75**, which is more stable than the analogue **53** with *i*-Pr wingtip substituents (*cf* Scheme 19), catalyses the C–H bond activation and catalytic

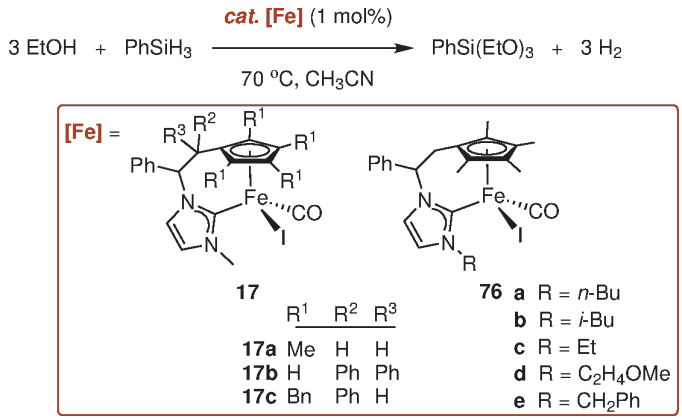
borylation of furans and thiophenes (Scheme 26).[105] The C–B bond forming reaction is regioselective, occurring at the 2- or 5-position, depending on steric factors. Mechanistic investigations reveal the crucial role of the *tert*-butyl ethylene additive, which presumably inserts into the Fe–H bond of a putative hydride intermediate, thus recycling the catalyst to a new active alkyl intermediate. The alkyl complexes are essential for C–H activation of the heteroarenes.



Scheme 26. *Borylation of furans (E = O) and thiophenes (E = S) catalysed by the coordinatively unsaturated iron complex **75**.[105]*

5.2. Dehydrogenative silylation of alcohols

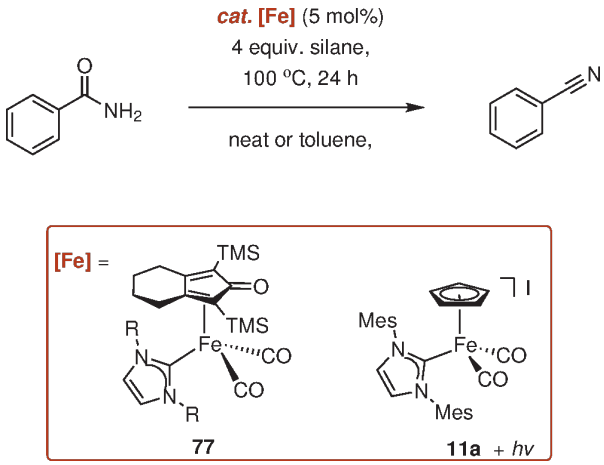
Royo *et al*. have disclosed the first example of NHC iron-catalysed dehydrogenative silylation of alcohols (Scheme 27).[116] Using relatively low catalyst loadings of 1 mol% and $PhSiH_3$, as reducing agent, complexes **17a,b** and **76a–e** give good to excellent conversions of ethanol to triethoxyphenylsilane. The best activity is achieved when the carbene contains *n*-butyl or *i*-butyl wingtip substituents (quantitative yields within 8 h) while longer reaction times are required with other wingtip groups in the catalyst precursor. No significant difference in activity is observed when changing the supporting ligand from Cp to Cp*. The transformation is versatile and tolerates a range of different silanes and alcohols.



Scheme 27. *Dehydrogenative silylation of alcohols catalysed by cyclopentadienyl-tethered imidazolylidene iron(II) complexes* ***17*** *and* ***76****.[116]*

5.3. Dehydration of amides

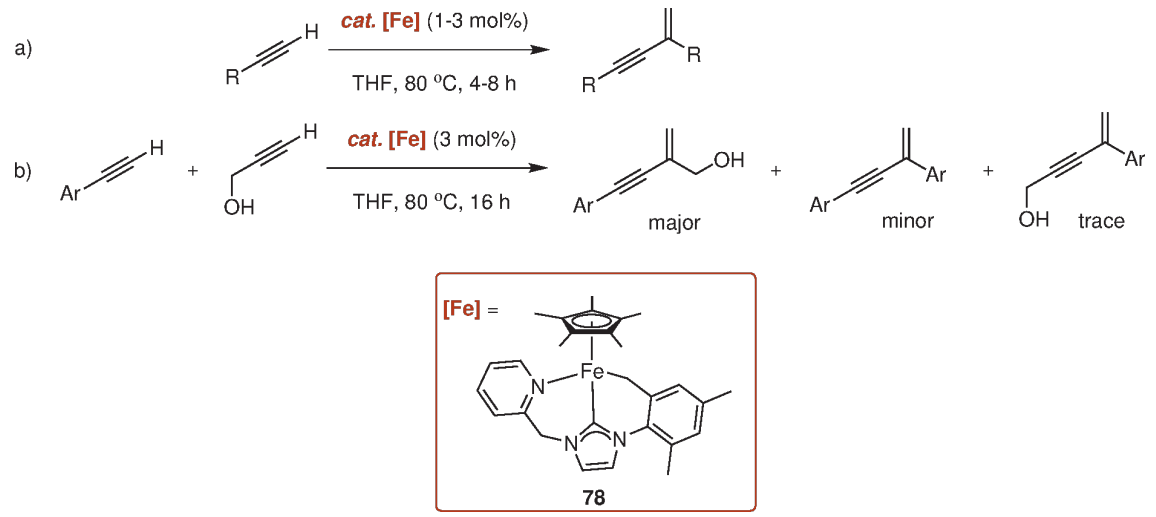
Dehydration of amides to nitriles catalysed by an iron complex using hydrosilanes has first been reported by Beller in 2009.[117] Following this work, Darcel and Sortais have shown that the NHC iron complex **11a** also catalyses this transformation (Scheme 28).[110] When using a typical hydrosilylation protocol, benzamide is quantitatively converted to benzonitrile in the presence of $PhSiH_3$ and 5 mol% NHC iron complex. In addition to relatively high catalyst loadings, rather forcing conditions are required (100 °C for 24 h). With the new Knölker-type NHC complexes **77** (Scheme 28),[118] PMHS can be utilised as a cheaper silane. Decreasing the temperature, catalyst loading, or the silane equivalents significantly reduces the final conversions. The catalytically beneficial role of the NHC and cyclopentadienone ligands is supported by the poor activity of $[(IMes)Fe(CO)_4]$ and the inactivity of the tricarbonyl analogue of complex **77**. Beller[117] has proposed a mechanism for this iron-catalysed transformation that is related to the analogous process mediated by ruthenium.[119] Specifically, two equivalents of silane are presumed to react with the amide substrate with the evolution of hydrogen gas. The ensuing bis(silyl)amide intermediate, which is in equilibrium with a *N*,*O*-bis(silyl)imidate, is then proposed to eliminate disiloxane to afford the nitrile product. Contrasting to this reactivity pattern, preliminary studies using the iron(0) complex **8** have shown that under very similar reaction conditions, amides are reduced to amines.[56]



Scheme 28. *Dehydration of primary amides to nitriles catalysed by piano-stool NHC iron complexes* ***11a*** *and 77.[110,118]*

5.4. Dimerisation of terminal alkynes

The well-defined Cp* iron complex **78** bearing an *N*,*C*,*C*-chelating imidazolylidene ligand catalyses the *gem*-specific dimerisation of terminal alkynes (Scheme 29).[120] With relatively low catalyst loadings of 1–3 mol%, aromatic and aliphatic terminal alkynes are homo-coupled in excellent yields within 4 h at 80 °C. The catalytic reaction tolerates a wide range of substrates, including alkynes with –OH and –NH functional groups. Cross-dimerisation is strongly promoted when a mixture of propargyl alcohol and arylacetylenes are used as substrate (Scheme 29b). The authors attribute the strong bias towards the cross-coupled product (up to 15:1 ratio of cross- *vs*. homodimerisation) to heteroatom stabilisation of the π*-orbital of propargyl alcohol, which controls the chemo- and regioselectivity. The proposed mechanism involves first dissociation of the picolyl moiety, followed by coordination and subsequent C–H activation of the alkyne across the Fe–CH_2 bond to form a σ-complex. Migratory insertion of a second alkyne substrate into the Fe–C_{alkyne} bond affords the C–C coupled product, which is eliminated by a cyclometallation process, which regenerates the active catalyst.



Scheme 29. *a) Homodimerisation and b) cross-dimerisation of alkynes catalysed by the N,C,C-chelating imidazolylidene complex* ***78*** *(R = e.g.* Ph, Bu, $SiMe_3$; *Ar = p-R'C_6H_4 with R' = CH_3, F, OMe, NMe_2).[120]*

6. Conclusions

Even though barely explored only two decades ago, the $[CpFe(NHC)]^+$ unit has rapidly emerged as a highly versatile synthon for synthesis and catalysis. In particular in the last few years, a variety of bond activation reactions have been disclosed, both stoichiometric such as heterocyclic C–H bond activation, as well as catalytic. In particular, catalytic transfer hydrogenation and hydrosilylation reactions are catalysed by appropriately tailored piano-stool NHC iron catalysts with high efficiency. Recently, also some carbon-carbon bond forming reactions have been disclosed, though this area of catalytic application is in its infancy at best for $[CpFe(NHC)]^+$-type complexes.

Various challenges remain and provide formidable opportunities both for catalytic application as well as for gaining fundamental insights into reactivity properties. For example, catalytic loadings are usually quite high and suggest a relatively low stability of the catalytically active species. Furthermore, chiral modifications of the catalyst precursors for asymmetric substrate reduction constitutes an appealing avenue that has not been explored at all so far. While cross-coupling reactions have been successfully implemented in iron chemistry, the $[CpFe(NHC)]^+$, synthon has not been exploited significantly in such processes. Finally, oxidative transformations have been elusive so far with such iron systems as catalyst precursors, even though higher-valent iron centres should be stabilised by the NHC ligand. A robust Fe–C(NHC) bond will be a critical parameter that needs to be addressed in order to enable such catalytic applications, for example through sophisticated ligand design. These prospects for

further development illustrate both the challenges and the high attractiveness of piano-stool NHC iron complexes for catalytic applications and beyond.

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